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Attached is a copy of requested pages 278 and 279 in Serial No. 10/054,462.

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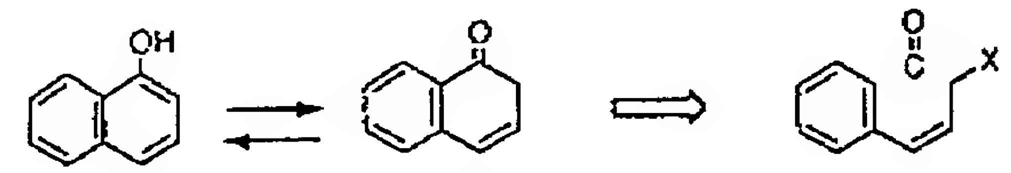
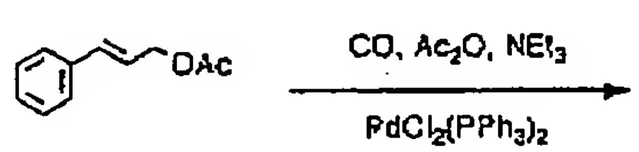


Scheme 4.

The products of these reactions have been limited to a narrow range of compounds such as indanones and quinones. In addition, very drastic reaction conditions are required in most cases. These limitations have prevented the cyclocarbonylations of aromatic systems from systematic application in organic syntheses.

Based on the background described above, we selected 1-naphthol as the first synthetic target molecule because it can be regarded as a hiding member of cyclic aromatic ketone (Scheme 4). Simple retrosynthetic analysis leads to an idea that readily available cinnamyl compounds are suitable substrates.

Although attempted carbonylation of cinnamyl acetate (**1a**) in the presence of NEt_3 and a catalytic amount of $PdCl_2(PPh_3)_2$ gave no isolable and characterizable product, we found that addition of Ac_2O is very effective to make the reaction clean. 1-Naphthol, the expected product was isolated as the corresponding acetate. Thus, **1a** and cinnamyl bromide (**1b**) were smoothly cyclocarbonylated to form 1-naphthyl acetate (**2a**) in 74% and 41% yield, respectively, when heated at 160 °C under 60 atm of CO in the presence of Ac_2O, NEt_3, and a catalytic amount of $PdCl_2(PPh_3)_2$ (Eq. 1).[10]



1a 2a 74% (1)

Synthesis of 1-naphthyl acetate. Cinnamyl acetate (**1a**, 10 mmol), Ac_2O (20 mmol), NEt_3 (20 mmol), $PdCl_2(PPh_3)_2$ (0.07 mmol), and benzene (8 mL) were charged in a stainless steel autoclave under a nitrogen atmosphere. The reactor was closed, pressurized to 60 atm with CO, heated quickly up to 160 °C, and kept at this temperature for 1 h with magnetic stirring. The reactor was then cooled to room temperature and the gas purged. GC analysis of the reaction mixture indicated that 1-naphthyl acetate was formed in 74% yield based on the **1a** charged (92% conversion). The reaction mixture was washed with 1 N aqueous HCl, aqueous $NaHCO_3$, and water, and the resulting solution was evaporated to give a brown oil. The oil was purified by silica gel column chromatography followed by bulb-to-bulb distillation to give 1-naphthyl acetate in 46% yield.

Addition of NEt_3 is essential to obtain **2a** in good yields. The base is necessary to quench the acetic acid (and HBr) formed, and to promote the acetylation of

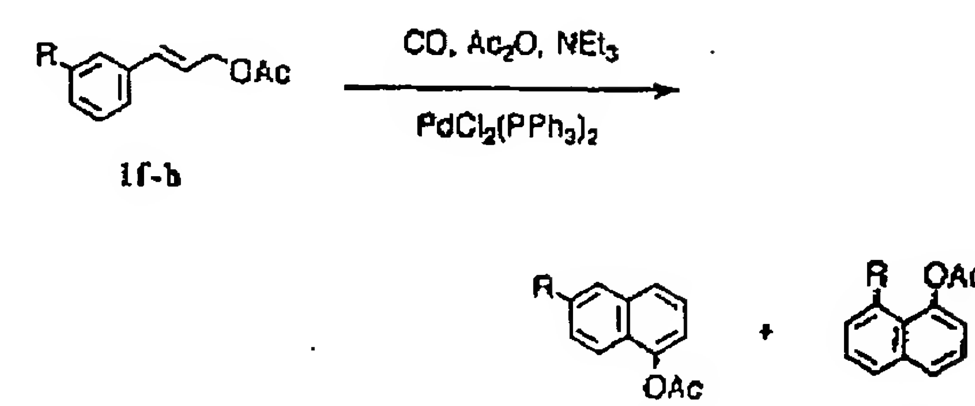
Table 1. Effect of Catalyst on the Cyclocarbonylation of Cinnamyl Acetate (**1a**)[a]

Catalyst	*Conv. (%)*	*Yield (%)*[b]
$PdCl_2(PPh_3)_2$	92	74
$Pd(CO)(PPh_3)_3$	88	88
$Pd(PPh_3)_4$	73	70
$PtCl_2(PPh_3)_2$	66	44
$NiBr_2(PPh_3)_2$	14	14
$Ru_3(CO)_{12}$	9	9
$Co_2(CO)_8$	7	5
$RhCl(CO)(PPh_3)_2$	2	2

Notes: [a]Reaction conditions: cinnamyl acetate 10 mmol, catalyst 0.07 mmol, Ac_2O 20 mmol, NEt_3 20 mmol, benzene 8 mL, CO 60 atm, 160 °C, 1 h.
[b]Based on the cinnamyl acetate charged.

1-naphthol. The reaction proceeded smoothly at 160 °C to give **2a** in good yield, but lower reaction temperatures resulted in a drastic decrease in the yield of **2a** and formation of a complex mixture of unidentified high-boiling compounds.

A variety of palladium monophosphine complexes were found to be effective catalysts for cyclocarbonylation of **1a** (Table 1). Zero-valent palladium–phosphine complexes such as $Pd(PPh_3)_4$ and $Pd(CO)(PPh_3)_3$ were the most effective catalysts. $PdCl_2(PPh_3)_2$ was also conveniently used under usual conditions (0.7–5 mol %), but analogous complexes such as $PdCl_2(PMePh_2)_2$ and $PdCl_2(PMe_2Ph)_2$ showed somewhat higher catalytic activity under low catalyst concentration conditions. In contrast, none of $Pd(OAc)_2$, $PdCl_2(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$), and $PdCl_2(AsPh_3)_2$ showed catalytic activity. Not only palladium complexes but also $PtCl_2(PPh_3)_2$ was an effective catalyst. Compound **2a** was also formed by the catalysis of $NiBr_2(PPh_3)_2$, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $RhCl(CO)(PPh_3)_2$, but the yields were quite low. Based on these results, we concluded that smooth cyclocarbonylation of **1a** to give **2a** requires a reaction temperature of about 160 °C and the presence of Ac_2O, NEt_3, and a catalytic amount of palladium or platinum monophosphine complexes.



1f-h (2) 2f-h 2f-h'